

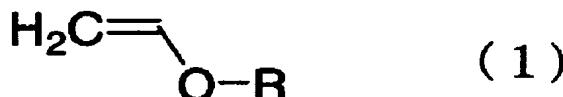
[Document Name] SPECIFICATION

[Title of the Invention] FLUORINE-CONTAINING VINYL ETHERS,
FLUORINE-CONTAINING POLYMERS USING SAME, AND RESIST
MATERIALS USING FLUORINE-CONTAINING POLYMERS

5 [Scope of Claims]

[Claim 1] A fluorine-containing vinyl ether represented by the following general formula (1),

[Chemical Formula 1]

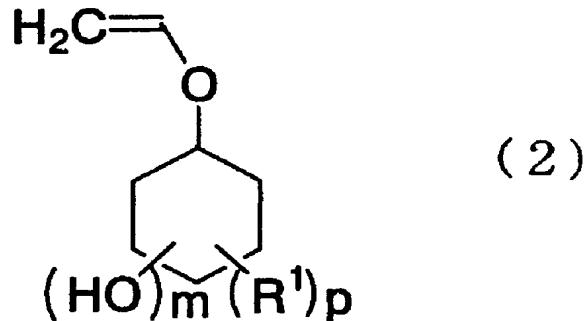


10 (In the formula, R represents an organic group containing at least one fluorine atom and having a cyclic structure.).

[Claim 2] A fluorine-containing vinyl ether according to claim 1, wherein R has at the same time the cyclic structure that is selected from cyclopentane ring, cyclohexane ring, norbornene ring, aromatic rings and tricyclodecane ring; and one or at least two substituents that are selected from $(-\text{OH})_m$, $(-\text{R}^1)_n$, and $-\text{COOR}^4$, (Herein, R^1 is one or at least two substituents selected from $-\text{F}$, $-\text{CF}_3$, and $-\text{R}^2\text{C}(\text{CF}_3)_2\text{OR}^3$. R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile group. R^4 is H, a $\text{C}_1\text{-C}_{15}$ alkyl group, or a $\text{C}_1\text{-C}_{15}$ substituent containing an ether bond. m is 0 or 1, and n is an integer of 1-8.).

20 [Claim 3] A fluorine-containing vinyl ether according to claim 1 or 2,
which is represented by the following general formula (2),

[Chemical Formula 2]

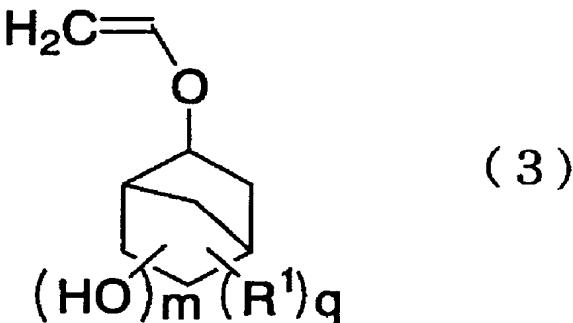


(In the formula, R¹ is one or at least two substituents selected from –F,

$-CF_3$, and $-R^2C(CF_3)_2OR^3$. R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile group, and p is an integer of 1-5, and m is 0 or 1.)

[Claim 4] A fluorine-containing vinyl ether according to claim 1 or 2, which is represented by the following general formula (3),

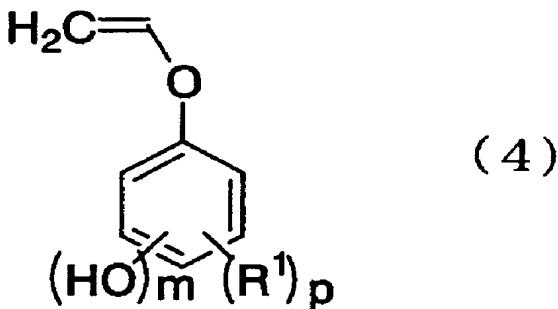
5 [Chemical Formula 3]



(In the formula, R^1 is one or at least two substituents selected from $-F$, $-CF_3$, and $-R^2C(CF_3)_2OR^3$. R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile group. q is an integer of 1-4, and m is 0 or 1.).

10 [Claim 5] A fluorine-containing vinyl ether according to claim 1 or 2, which is represented by the following general formula (4),

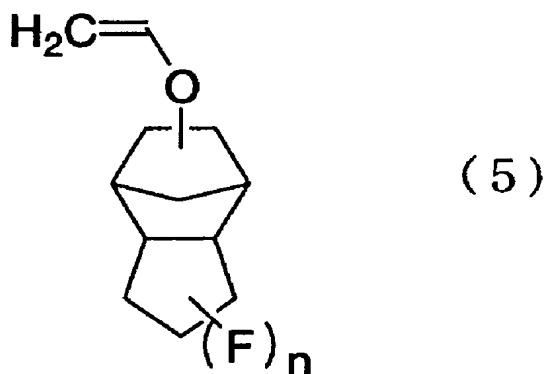
[Chemical Formula 4]



(In the formula, R^1 is one or at least two substituents selected from $-F$,

15 $-CF_3$, and $-R^2C(CF_3)_2OR^3$. R^2 is CH_2 or C_2H_4 , and R^3 is H or an acid-labile group. p is an integer of 1-5, and m is 0 or 1.)

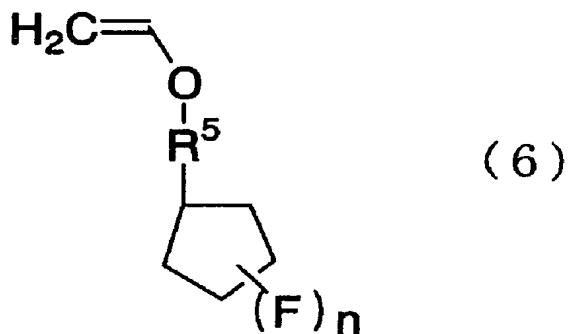
[Claim 6] A fluorine-containing vinyl ether according to claim 1 or 2, which is represented by the following general formula (5),



(In the formula, n is an integer of 1-8.).

[Claim 7] A fluorine-containing vinyl ether according to claim 1 or 2, which is represented by the following general formula (6),

5 [Chemical Formula 6]



(In the formula, R⁵ is a C₀-C₅ alkyl group, and n is an integer of 1-8.).

[Claim 8] A fluorine-containing vinyl ether according to any one of claims 1-7, which comprises a hexafluoroisopropanol unit represented by the

10 following general formula (7),

[Chemical Formula 7]



[Claim 9] A fluorine-containing polymer or fluorine-containing copolymer using a fluorine-containing vinyl ether according to any one of claims 1-8.

[Claim 10] A resist material using a fluorine-containing polymer according to claim 9.

[Detailed Description of the Invention]

[0001]

5 [Technical Field to which the Invention Belongs]

The present invention relates to fluorine-containing vinyl ethers, fluorine-containing polymers using the same, and resist materials using the fluorine-containing polymers.

[0002]

10 [Prior Art]

Hitherto, fluorine-containing polymers have been used in various fields, since they are superior in heat resistance and chemical resistance. In particular, amorphous fluorine-containing polymers have been used and studied in the fields of optical fiber and resist material due to their high

15 transparency in addition to those capabilities (for example, see Patent Publication 1). To their applications, the introduction of fluorine atoms lowers refractive index or improves transparency of the vacuum ultraviolet region light. As the development of resist materials is described (for example, see Non-patent Publication 1), now, a major resist type is a
20 positive-type resist material, in which an acid is generated by light irradiation and then solubility of a resin in alkali aqueous solution is increased along with a chemical change of the resin by an action of the acid as a catalyst. However, in the trend toward shorter wavelength of light to finer processing, there are problems that novolak resins, acrylic resins and
25 the like used in current resists are insufficient in transparency. Namely, there are a demand for polymers that contain fluorine atoms, do not contain structures such as carbonyl, have heat resistance, and are superior in solubility in various solvents, and a demand for monomers for synthesizing the same.

30 [0003]

[Patent Publication 1]

Japanese Patent Application Publication 2002-201231

[Non-patent Publication 1]

Y. Kamon et al., J. Photopolym. Sci. Technol., 15, 535 (2002)

[0004]

5 [Task to be solved by the Invention]

It is a task of the present invention to provide monomers that can be a raw material of polymer materials, which are low in light scattering and absorption and are required to have high transparency, transparent fluorine-containing polymers using the same, and resist materials using the
10 fluorine-containing polymers.

[0005]

[Means for solving the Task]

As a result of an eager examination, the present inventors have found that novel fluorine-containing vinyl ethers are effective for solving the
15 task, thereby reaching the present invention. Specifically, it was found that the novel fluorine-containing vinyl ethers of the present invention are capable of producing homopolymers and copolymerizing with various monomers, and that the resulting fluorine-containing polymers dissolve in various organic solvents and at the same time have high transparency.

20 [0006]

That is, the present invention provides fluorine-containing vinyl ethers represented by the following general formula (1), fluorine-containing polymers using the same, and resist materials using the fluorine-containing polymers.

25 [0007]

[Chemical Formula 8]



(In the formula, R represents an organic group containing at least one fluorine atom and having a cyclic structure.).

In the following, the present invention is described in detail. The fluorine-containing vinyl ether of the present invention is a fluorine-containing vinyl ether represented by the following general formula (1).

5 [0009]

[Chemical Formula 9]



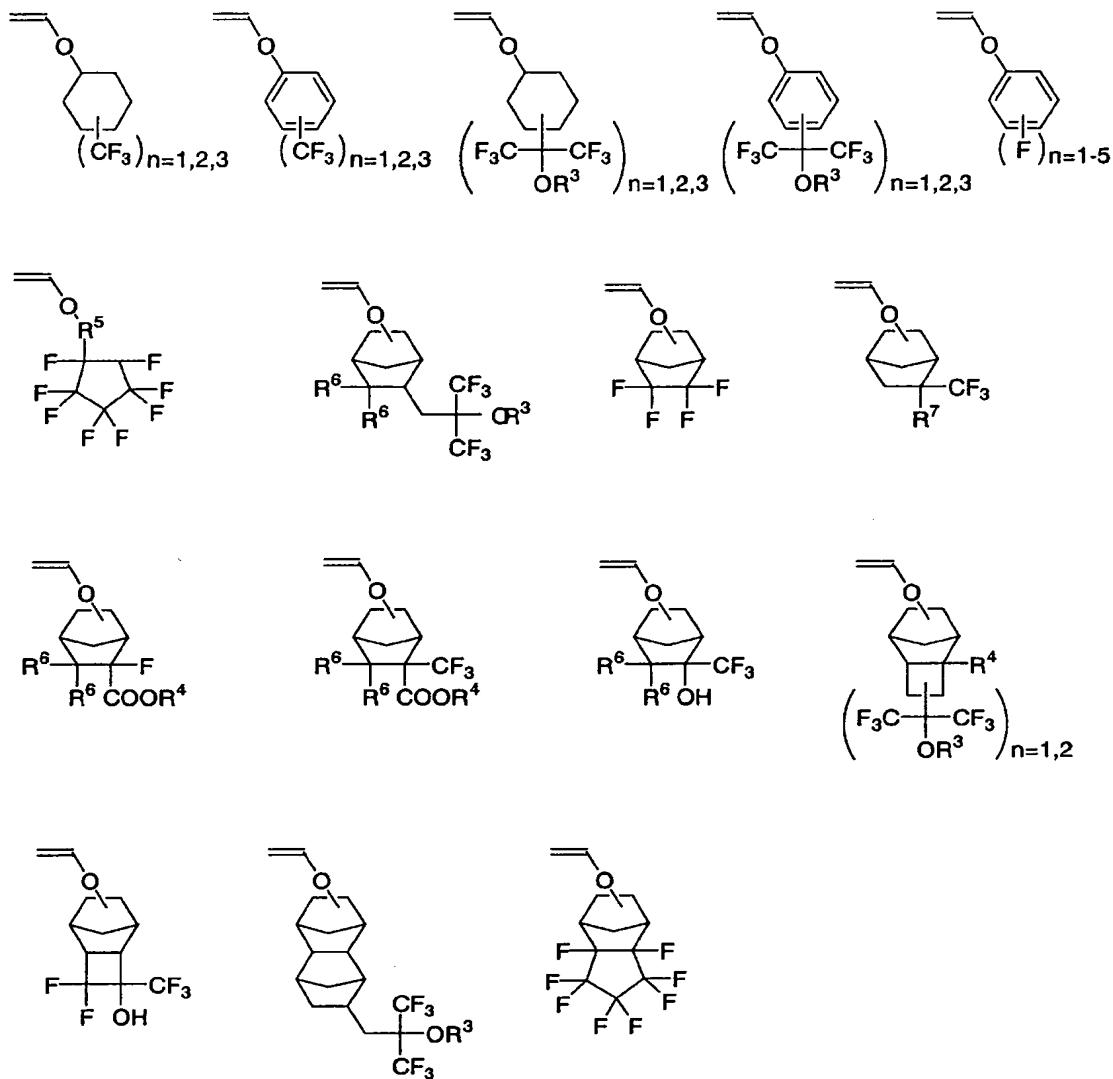
[0010]

(In the formula, R represents an organic group containing at least one
10 fluorine atom and having a cyclic structure.).

As they are more specifically exemplified, those of the following structural formulas are cited.

[0011]

[Chemical Formula 10]



(R³: H or an acid-labile group.)

(R⁵: a C₀-C₅ alkyl group.)

5 (R⁶: H or F)

(R⁷: CF₃, OH, CO₂H, CO₂R⁸, or OCOR⁸)

(R⁸: C₁-C₁₅ alkyl group))

(R⁴: H, a C₁-C₁₅ alkyl group, or a C₁-C₁₅ substituent having an ether bond)

[0012]

10 Of these, those containing a hexafluoroisopropanol unit

(-C(CF₃)₂-OH) or unit (-C(CF₃)₂-OR³) derived from hexafluoroisopropanol serve to improve adhesion to substrate when they have become polymers.

Herein, R³ is a hydrogen or acid-labile group. The acid-labile group optionally contains a hetero atom(s) such as oxygen. As the acid-labile group is exemplified, t-butoxycarbonyl group, methoxymethyl group, 2-methyl-2-adamantyl ester group, 2-ethyl-2-adamantyl ester group and the like are cited. Vinyl ethers containing a structure such as bicyclo[2.2.1]heptane or tricyclodecane are preferable ones, since light absorption derived from a double bond is low when they become polymers and since the polymers are superior in heat resistance.

[0013]

Various known processes can be used for producing the fluorine-containing vinyl ethers of the present invention. As they are exemplified, it is a process of obtaining that by treating a fluorine-containing alcohol with an alkali metal, followed by a reaction with acetylene or vinyl halide. As the alkali metal then, it is possible to use various alkali metal compounds. For example, they are sodium hydride, potassium hydride, sodium hydroxide, potassium hydroxide, potassium carbonate, and the like.

[0014]

It is known to synthesize vinyl ethers by vinyl exchange reaction using Pd as catalyst. In this vinyl exchange reaction, the reaction is conducted in the presence of a vinyl ether or alcohol to obtain a new vinyl ether. In particular, the vinyl exchange reaction using Pd as catalyst is used as a preferable synthesis process, since the reaction conditions are mild and since side reactions do not easily occur. As Pd then, it is possible to use a bivalent Pd such as palladium acetate (Pd(OAc)₂). It is also possible to use a ligand together therewith for the purpose of controlling the reaction activity of Pd. The type of this ligand is not particularly limited. Nitrogen-containing bidentate ones are cited as preferable ones since the amounts of the production of by-products are small. As they are exemplified, they are 2,2'-bipyridyl, 1,10-phenanthroline and the like. The preparation of Pd and the ligand can previously be conducted. However,

its object is achieved even by separately adding both to the reaction system upon the reaction to make a ligand during the reaction.

[0015]

It is possible to use a solvent upon the reaction. They are not particularly limited so long as they do not interfere with the target reaction. Examples are common organic solvents such as tetrahydrofuran, diethyl ether and dimethylformamide. It is possible to use a vinyl ether that becomes the substrate of the vinyl exchange reaction, as the solvent. That is, a fluorine-free vinyl ether is used as the reaction substrate and as the reaction solvent in the present invention, and it is reacted with a fluorine-containing alcohol, thereby obtaining a fluorine-containing vinyl ether. Although the temperature upon synthesis is not particularly limited, it is preferably in a range of -80°C to 200°C in view of reactivity and handling easiness of peripheral devices. More preferably, it is in a range of -30°C to 150°C. The reaction product can be separated and purified by a common process. As they are exemplified, concentration, extraction, distillation, recrystallization, filtration, and column chromatography are cited. It may be conducted by combining these.

[0016]

Next, a fluorine-containing polymer of the present invention is described. A fluorine-containing polymer of the present invention is a polymer containing a unit formed of a fluorine-containing vinyl ether in the present invention. Homopolymer or copolymer corresponds to that.

[0017]

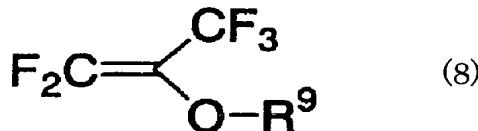
Comonomer in the copolymer can be used without particular limitation. Several kinds can also be used in combination. As they are exemplified, α -olefins (e.g., ethylene and propylene), cyclic olefins (e.g., norbornene and cyclohexene), vinyl ethers other than that of the invention, vinyl esters, acrylic or methacrylic acid, acrylic or methacrylic ester, α -trifluoromethylacrylic acid, α -trifluoromethylacrylic ester, allyl ether, styrene, vinyl silane, anhydrous maleic acid, and the like are cited. They

may contain fluorine atoms, heteroatoms (e.g., oxygen), functional groups, cyclic structure organic groups (e.g., adamantyl group), and reactive groups that are released by the action of acid. Furthermore, it is possible to use fluoroolefins such as tetrafluoroethylene, chlorotrifluoroethylene,

5 hexafluoroisobutene, hexafluoropropylene, trifluoroethylene, perfluorovinyl ether, octafluorocyclopentene, and an olefin represented by the following general formula (8). R⁹ is an alkyl group having a carbon number of from 1 to 15 and may contain a heteroatom(s) such as oxygen.

[0018]

10 [Chemical Formula 11]



[0019]

An arbitrary range is selected without particular limitation for the ratio of the fluorine-containing vinyl ether to the comonomer in those

15 copolymers. It is preferable that the copolymer contains 0.1 mol% or greater of a unit based on the fluorine-containing vinyl ether of the present invention, in order to show high transparency of the fluorine-containing polymer of the present invention. More preferably, it is 1 mol% or greater.

[0020]

20 In number average molecular weight of the fluorine-containing polymer of the present invention, a range of 1,000 to 1,000,000 is generally appropriate. A range of 2,000 to 100,000 is preferably appropriate. If the molecular weight is less than that, it is insufficient in strength as polymer and inferior in heat resistance in the use as various materials. If the

25 molecular weight is greater than 100,000, it is inferior in solubility in solvent.

[0021]

The process of producing the fluorine-containing polymer of the present invention is not particularly limited. A known process such as

anionic polymerization, radical polymerization, cation polymerization or coordination polymerization is used. Preferably, radical polymerization is used. As the polymerization manner then, a known method such as bulk polymerization, solution polymerization, suspension polymerization or emulsion polymerization can be used.

5 [0022]

The temperature of the polymerization reaction can be suitably set depending on the polymerization process, polymerization manner, the type of the polymerization initiator, and the like. Specifically, it is 20-200°C,

10 preferably 40-120°C.

[0023]

Examples of the radical polymerization initiator are not particularly limited. As examples, azo-series compounds, peroxide-series compounds and redox-series compounds are cited.

15 [0024]

Solvent may be used in the polymerization reaction upon producing the fluorine-containing polymer of the present invention. Although the solvent is not particularly limited, it is preferably one that does not greatly interfere with the polymerization. Its examples are ketone-series solvents such as acetone; aromatic-series solvents such as toluene; hydrocarbon-series solvents such as cyclohexane; alcohol-series solvents such as isopropyl alcohol; and ester-series solvents such as butyl acetate. Furthermore, it is possible to use a molecular weight adjusting agent, such as mercaptan, together therewith.

25 [0025]

As the emulsifying agent upon conducting the emulsion polymerization, it is possible to use an anion or nonion emulsifying agent or both. Although the radical initiator then is not particularly limited, a water-soluble initiator such as persulfate can preferably be used.

30 [0026]

The suspension stabilizer upon conducting the suspension polymerization is not particularly limited. It is possible to use a generally used, water-soluble polymer such as methylcellulose.

[0027]

5 The fluorine-containing vinyl ether of the present invention is useful as a raw material monomer of transparent polymer compounds for coating use. The fluorine-containing polymers synthesized using that as the raw material can be applied as various transparent polymers.

[0028]

10 That is, the fluorine-containing polymers of the present invention are useful as resist materials for producing semiconductors and as anti-reflection film materials. Furthermore, they are useful as core materials, cladding materials, covering materials, and optical bonds for resin optical fibers and optical waveguides.

15 [0029]

In resist materials according to the present invention, the method of using the fluorine-containing polymer in the present invention is not particularly limited. As its example, it is applied as a polymer compound that changes solubility in alkali aqueous solution by the generation of acid
20 or amine. Its type can be applied to both of positive-type and negative-type. As an acid-labile group usable then, its object is achieved by introducing it into the fluorine-containing vinyl ether or the copolymerization component or by introducing it into them in combination.

[0030]

25 Then, a resist can be constituted by an organic solvent, a photoacid generator and an additive in addition to the fluorine-containing polymer in the present invention. It is possible to mix other polymers into the solution by an arbitrary ratio to use a resin blend.

[0031]

30 Organic solvent dissolves the fluorine-containing polymer in the present invention to make it into a coating material. Although the organic

solvent is not particularly limited, its examples are ketones such as acetone and methyl ethyl ketone; polyhydric alcohols and their derivatives such as ethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, and propylene glycol monomethyl ether acetate; ethers such as

- 5 tetrahydrofuran and dioxane; esters such as ethyl acetate, butyl acetate, methyl lactate, and ethyl lactate; aromatic solvents such as xylene and toluene; and fluorine-series solvents such as fleon. These can be used alone or in combination.

[0032]

- 10 The photoacid generator is not particularly limited. It can be used by selecting an arbitrary one from those used as acid generators of chemically amplified resists. As examples of such acid generator, bisulfonyldiazomethanes, nitrobenzyl derivatives, onium salts, halogen-containing triazine compounds, cyano group-containing
15 oximesulfonate compounds, and other oximsulfonate compounds are cited. These acid generators may be used alone or may be used in combination of at least two types. Its content is generally used in a range of 0.5-20 parts by weight relative to 100 parts by weight of the polymer compound.

[0033]

- 20 Examples of other additives are solubility inhibitor, plasticizer, stabilizer, coloring agent, light amplifier, surfactant, tackifier, leveling agent, defoaming agent, adhesion enhancing agent, quencher, and the like.

[0034]

- The use of a resist material of the present invention can be
25 conducted by a method similar to conventional photoresist techniques. For example, in case that the fluorine-containing polymer of the present invention is applied as a polymer compound that changes solubility in alkali aqueous solution by acid generation, a solution of resist composition is applied to a silicon wafer by spin coating, followed by drying and film
30 formation, and this is irradiated with a pattern through a mask by a light

exposure apparatus. By subjecting this to heating and alkali development, a desired pattern can be formed on the resin layer.

[0035]

In the use of anti-reflection film material, it can be achieved by
5 applying a solution of the fluorine-containing polymer of the present invention on a substrate, followed by drying and according to need heating, thereby forming a film to have a film thickness and a film structure showing anti-reflection capability.

[0036]

10 [Embodiments of the Invention]

Next, the present invention is explained in more detail by examples, but the present invention is not limited at all to these.

[0037]

[Examples]

15 [Synthesis Example 1]

A 100mL glass container was charged with 11.2g of palladium acetate and 1L of toluene to prepare a solution. 8g of bipyridyl and 200mL of toluene solution, which had separately been prepared, were gradually added thereto, followed by stirring for 10 minutes. The obtained
20 precipitate was filtered, washed with ether, and then recrystallized in dichloromethane of 500mL. 3hr later, the crystals were taken out by filtration treatment, followed by vacuum drying for 12hr, thereby preparing a Pd catalyst.

[0038]

25 [Example 1]

A 100mL glass container was charged with 2.96g of an alcohol 1 shown in the following, 0.19g of the Pd catalyst prepared by Synthesis Example 1, and 19mL of ethyl vinyl ether, followed by stirring under cooling in water bath for 24hr. The reaction mixture liquid was filtered through
30 Cellite, followed by washing with water and saturated brine, drying with anhydrous magnesium sulfate, and distilling the solvent off, thereby

obtaining 1.7g of the target vinyl ether 1 shown in the following, through silica gel chromatography. The vinyl ether 1 is a mixture of two kinds of stereoisomers. The obtained compound was identified by nuclear magnetic resonance and mass spectroscopy.

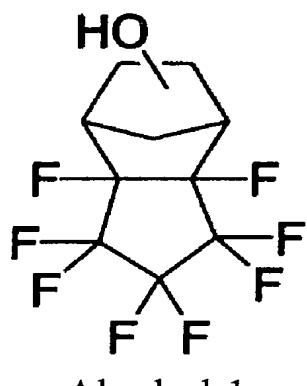
5 Property Data

¹H NMR (CDCl₃, TMS standard, 400MHz)

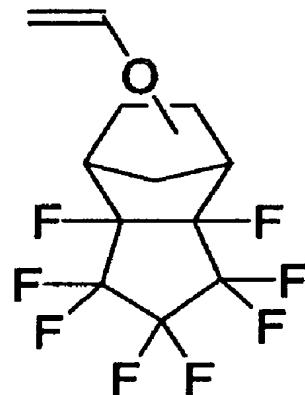
δ 1.70-1.73 (m, 2H), 2.0-2.5 (m, 2H), 2.8-3.8 (m, 2H), 4.1-4.5 (m, 3H), 6.29 (dd, J=6.8, 14.4Hz, 0.4H) Isomer 1, 6.31 (dd, J=6.8, 14.4Hz, 0.6H) Isomer 2
MS m/z (%) 322 (M⁺, 100), 239(36), 95(45)

10 [0039]

[Chemical Formula 12]



Alcohol 1



Vinyl ether 1

[0040]

[Example 2]

15 A 100mL glass container was charged with 2.36g of an alcohol 2 shown in the following, 0.19g of the Pd catalyst prepared by Synthesis Example 1, and 26mL of t-butyl vinyl ether, followed by stirring at reflux temperature for 4hr. After that, an operation similar to that of Example 1 was conducted, thereby obtaining 1.2g of the target vinyl ether 2 shown in
20 the following. The obtained compound was identified by nuclear magnetic resonance and mass spectroscopy.

Property Data

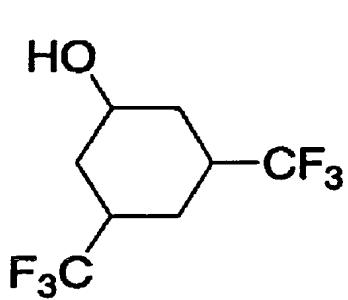
¹H NMR (CDCl₃, TMS standard, 400MHz)

δ 1.3-1.4 (m, 3H), 2.1-2.3 (m, 3H), 2.32-2.36 (m, 2H), 3.72-3.83 (m, 1H), 4.11 (dd, J=2.0, 6.6Hz, 1H), 4.34 (dd, J=2.0, 14.0Hz, 1H), 6.30 (dd, J=6.6, 14.0Hz, 1H)

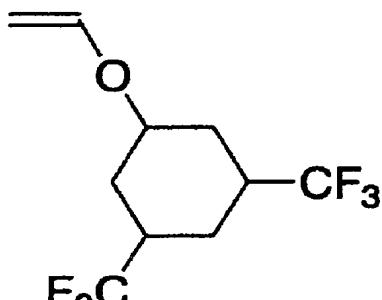
5 MS m/z (%) 262 (M⁺, 47), 199(75), 109(100)

[0041]

[Chemical Formula 13]



Alcohol 2



Vinyl ether 2

[0042]

10 [Example 3]

A 100mL glass container was charged with 2.92g of an alcohol 3 shown in the following, 0.19g of the Pd catalyst prepared by Synthesis Example 1, and 19mL of ethyl vinyl ether, followed by stirring under cooling in water bath for 24hr. After that, an operation similar to that of Example 1 was conducted, thereby obtaining 1.2g of the target vinyl ether 3 shown in the following. The obtained compound was identified by nuclear magnetic resonance and mass spectroscopy.

Property Data

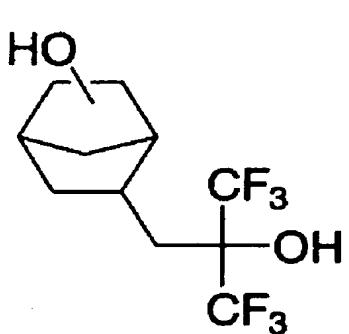
¹H NMR (CDCl₃, TMS standard, 400MHz)

20 δ 1.1-2.3 (m, 11H), 2.85-2.95 (m, 1H), 3.81-3.88 (m, 1H), 3.98-4.01 (m, 1H), 4.11-4.19 (m, 1H), 6.31 (dd, J=6.8, 14.4Hz, 1H)

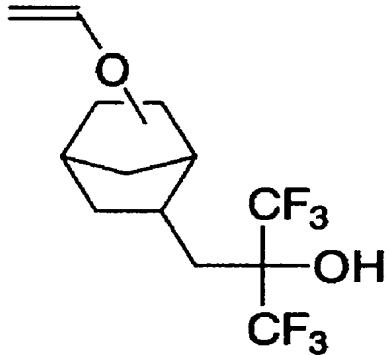
MS m/z (%) 318 (M⁺, 41), 275(100), 233(28)

[0043]

[Chemical Formula 14]



Alcohol 3



Vinyl ether 3

[0044]

[Example 4]

5 A 100mL glass container was charged with 4.32g of an alcohol 4 shown in the following, 0.19g of the Pd catalyst prepared by Synthesis Example 1, and 19mL of ethyl vinyl ether, followed by stirring under cooling in water bath for 3hr. After that, an operation similar to that of Example 1 was conducted, thereby obtaining 1.1g of the target vinyl ether 4 shown in
10 the following. The obtained compound was identified by nuclear magnetic resonance and mass spectroscopy.

Property Data

^1H NMR (CDCl_3 , TMS standard, 400MHz)

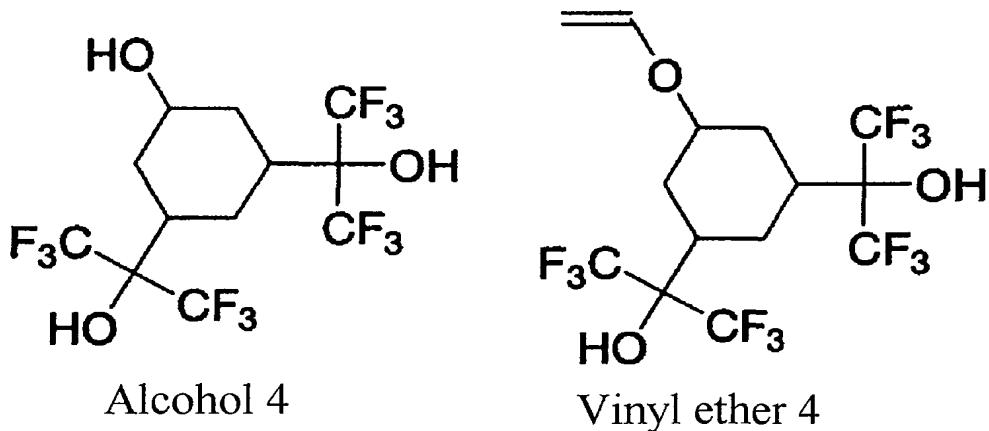
δ 1.1-1.6 (m, 4H), 2.31 (d, $J=14.0\text{Hz}$, 2H), 2.42-2.50 (m, 2H), 3.13 (s, 2H),

15 4.12 (dd, $J=1.6, 6.8\text{Hz}$, 1H), 4.29-4.32 (m, 1H), 4.35 (dd, $J=1.6, 14.0\text{Hz}$, 1H), 6.27 (dd, $J=6.8, 14.0\text{Hz}$, 1H)

MS m/z (%) 458 (M^+ , 1), 377(19), 247(100)

[0045]

[Chemical Formula 15]



[0046]

[Example 5]

A 10mL pressure-proof container was charged with 0.64g of the
5 vinyl ether 1, 0.007g of di-t-butylperoxypivalate, and 0.13g of butyl acetate,
followed by replacing the inside of the container with nitrogen. Then, the
reaction was conducted, while the reaction container was maintained at
60°C for 20hr. After the reaction, a polymer was reprecipitated from the
cooled reaction liquid with 30mL of n-hexane, followed by filtration and
10 vacuum drying, thereby obtaining 0.07g of a white-color polymer. The
weight average molecular weight of polystyrene conversion determined by
GPC measurement of the obtained polymer was 5,000. Furthermore, the
obtained polymer was soluble in propylene glycol monomethylacetate.
Light transmittance at 193nm wavelength of 100nm thickness conversion of
15 a coating film made from the solution was 98%.

[0047]

[Example 6]

A 10mL pressure-proof container was charged with 0.32g of the
vinyl ether 3 and 0.003g of azobisisobutyronitrile, followed by replacing the
20 inside of the container with nitrogen. Then, the reaction was conducted,
while the container was maintained at 60°C for 20hr. After the reaction,
0.5g of butyl acetate were added to the cooled reaction liquid to have a
homogeneous solution. A polymer was reprecipitated with 30mL of

n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.05g of a white-color polymer. The obtained polymer was found to have a weight average molecular weight of 5,600. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light
5 transmittance at 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 99%.

[0048]

[Example 7]

A 10mL pressure-proof container was charged with 0.48g of the
10 vinyl ether 1, 0.29g of α -trifluoromethylacrylic t-butyl ester (hereinafter abbreviated as TFMA-B), 0.01g of di-t-butylperoxypivalate, and 0.16g of butyl acetate, followed by replacing the inside of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, 1g of butyl acetate was added to the
15 cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated with 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.52g of a white polymer. The weight average molecular weight of polystyrene conversion determined by GPC measurement of the obtained polymer was 48,200. The molar
20 compositional ratio of the polymer determined from ^{19}F NMR peak strength was the vinyl ether 1 : TFMA-B = 47:53%. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 98%.

25 [0049]

[Example 8]

A 50mL pressure-proof container was charged with 0.48g of the vinyl ether 1, 0.32g of octafluorocyclopentene (hereinafter abbreviated as OFCPE), 0.01g of di-t-butylperoxypivalate, and 0.21g of butyl acetate,
30 followed by replacing the inside of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 60°C for

20hr. After the reaction, 1g of butyl acetate was added to the cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated with 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.41g of a white polymer. The weight average
5 molecular weight of the obtained polymer was 4,800. The polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 99%.

[0050]

10 [Example 9]

A 10mL pressure-proof container was charged with 0.48g of the vinyl ether 3, 0.29g of α -trifluoromethylacrylic t-butyl ester (hereinafter abbreviated as TFMA·B), 0.01g of di-t-butylperoxypivalate, and 0.16g of butyl acetate, followed by replacing the inside of the container with nitrogen.

15 Then, the reaction was conducted, while the container was maintained at 60°C for 20hr. After the reaction, 1g of butyl acetate was added to the cooled reaction liquid to have a homogeneous solution. A polymer was reprecipitated with 30mL of n-hexane, followed by filtration and vacuum drying, thereby obtaining 0.55g of a white polymer. The weight average
20 molecular weight of polystyrene conversion determined by GPC measurement of the obtained polymer was 7,600. The molar compositional ratio of the polymer determined from ^{19}F NMR peak strength was the vinyl ether 1 : TFMA·B = 50:50%. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at
25 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 99%.

[0051]

[Example 10]

The polymer obtained in Example 9 was dissolved in propylene
30 glycol monomethyl ether acetate to have a solid matter concentration of 10wt%. Then, triphenylsulfonium triflate made by Midori Kagaku Co., Ltd.

as an acid generator was dissolved to be in an amount of 2 parts by weight per 100 parts by weight of the polymer, followed by filtration with 0.2 micron membrane filter, thereby preparing a resist solution. This was applied to a silicon wafer by spin coating to obtain a resist film having a thickness of 500nm. After a preliminary baking at 110°C, a light exposure was conducted at 248nm with a KrF excimer laser, and then a post exposure baking was conducted at 120°C. Then, a development was conducted by a puddle method at 23°C for 1 minute using 2.38 wt% tetramethylammonium hydroxide aqueous solution, followed by washing with pure water and drying. As a result, the laser non-exposed portion was not dissolved by the tetramethylammonium hydroxide aqueous solution, but the laser-exposed portion was completely dissolved. Thus, a necessary positive-type behavior required as resist was observed.

[0052]

15 [Advantageous Effect of the Invention]

A polymer compound obtained by polymerization or copolymerization using a fluorine-containing vinyl ether compound of the present invention as a raw material monomer has characteristics that light scattering and absorption are low and that solubility in solvent is superior, and becomes useful as a transparent resist material suitable for coating.

[Document Name] Abstract

[Abstract]

[Task] It is to provide polymers that can be a base of resist materials, which are low in light scattering and absorption and are required to have
5 high transparency, and monomers that can be a raw material of the polymers.

[Solving Means] A fluorine-containing vinyl ether compound represented by the following general formula (1).

[Chemical Formula 1]



10 (In the formula, R represents an organic group containing at least one fluorine atom and having a cyclic structure.)

15 A fluorine-containing vinyl ether of the present invention is copolymerizable with various monomers, and the obtained fluorine-containing polymer is superior in solubility in solvent and transparency.

[Selected Drawing] None

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
038788.56253US

In re patent application of
Satoru KOBAYASHI et al.

Serial No. 10/533,788

Group Art Unit 1621

Filed: May 4, 2005

Examiner Rosalynd Keys

For: FLUORINE-CONTAINING VINYL ETHERS, THEIR POLYMERS,
AND RESIST COMPOSITIONS USING SUCH POLYMERS

TRANSLATOR'S DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, the below-named translator, certify that I am familiar with both the Japanese and the English language, that I have prepared the attached English translation of Japanese Patent Application No. 2003-022925, and that the English translation is a true, faithful and exact translation of the corresponding Japanese language paper.

I further declare that all statements made in this declaration of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of legal decisions of any nature based on them.

March 13, 2007
Date

Hideo Ohashi
Hideo Ohashi

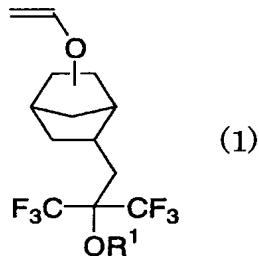
[Document Name] SPECIFICATION

[Title of the Invention] FLUORINE-CONTAINING COPOLYMERS
USING FLUORINE-CONTAINING VINYL ETHERS AND RESIST
MATERIALS USING FLUORINE-CONTAINING COPOLYMERS

5 [Scope of Claims]

[Claim 1] A fluorine-containing copolymer which is obtained by copolymerizing a fluorine-containing vinyl ether (A) represented by the general formula (1) with a monomer (B) as major monomer components, and in which the monomer (B) is at least one or two or more monomers selected
10 from acrylic esters or methacrylic esters.

[Chemical Formula 1]

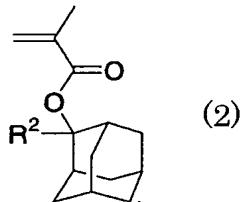


(In the formula, R¹ is -H or a C₁-C₈ alkyl group, and in the case of the alkyl group it may contain an oxygen atom.)

15 [Claim 2] A fluorine-containing copolymer according to claim 1, wherein the monomer (B) is an acrylic ester or methacrylic ester containing an acid-labile group.

[Claim 3] A fluorine-containing copolymer according to claim 1 or 2, wherein the monomer (B) is a methacrylic ester represented by the general
20 formula (2).

[Chemical Formula 2]

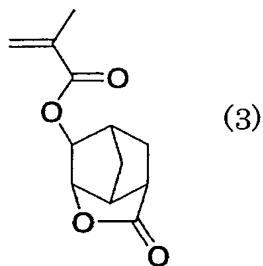


(In the formula R² is -CH₃ or -CH₂CH₃.)

[Claim 4] A fluorine-containing copolymer according to claim 1, wherein the monomer (B) is an acrylic ester or methacrylic ester having a lactone ring in at least a part of the structure.

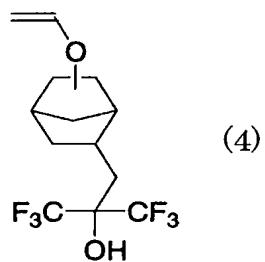
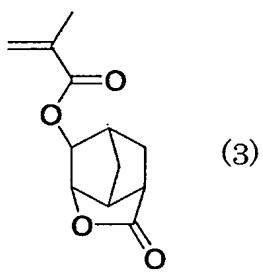
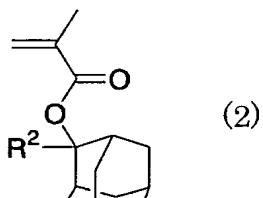
5 [Claim 5] A fluorine-containing copolymer according to claim 1 or 4, wherein the monomer (B) is a methacrylic ester represented by the structural formula (3).

[Chemical Formula 3]



10 [Claim 6] A fluorine-containing copolymer according to claim 1, which is obtained by copolymerizing three types of monomers represented by the following structural formulas (2), (3) and (4) as major components.

[Chemical Formula 4]



(In the formula R² is -CH₃ or -CH₂CH₃.)

[Claim 7] A resist composition using a fluorine-containing copolymer according to any one of claims 1-6.

5 [Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to fluorine-containing copolymers using fluorine-containing vinyl ethers, and resist materials using the

10 fluorine-containing copolymers.

[0002]

[Prior Art]

In the development of resist materials (for example, see Non-patent Publication 1), now, a major resist type is a positive-type resist material, in
15 which an acid is generated by light irradiation and then solubility of a resin

in alkali aqueous solution is increased along with a chemical change of the resin by an action of the acid as a catalyst. Along with the trend toward smaller semiconductor devices in recent years, there is a need for resist materials corresponding to the trend toward shorter wavelength of light to
5 finer processing. There has been a problem that novolak resins used in resists up to now are insufficient in transparency. However, it has been found that there is a possibility that acrylic-series resins have relatively good resist characteristics by research and development in recent years (for example, see Non-patent Publication 1). However, acrylic resins are still
10 insufficient in transparency due to the containment of a carbonyl structure that absorbs light of vacuum ultraviolet region. Further improvement is desired.

[0003]

On the other hand, fluorine-containing polymers have been used in
15 various fields, since they are superior in heat resistance and chemical resistance. In particular, amorphous fluorine-containing polymers have been used and studied in the fields of optical fiber and resist material due to their high transparency to vacuum ultraviolet region wavelength in addition to those capabilities (for example, see Patent Publication 1).
20 However, fluorine-containing monomers up to now have been inferior in copolymerizability with acrylic esters or methacrylic esters. Therefore, a combination of an acrylic-series monomer with a fluorine-containing monomer has been difficult. That is, in the present use, there is a desire for monomers that do not contain carbonyl structure, contain fluorine atom,
25 and are superior in copolymerizability with acrylic-series monomers, and for copolymers using the same.

[0004]

[Non-patent Publication 1]

Y. Kamon et al., J. Photopolym. Sci. Technol., 15, 535 (2002)

30 [Patent Publication 1]

Japanese Patent Application Publication 2002-201231

[0005]

[Task to be solved by the Invention]

It is a task of the present invention to provide transparent fluorine-containing copolymers that become polymer materials, which are low in light scattering and absorption and are required to have high transparency, and resist materials using the fluorine-containing copolymers.

[0006]

[Means for solving the Task]

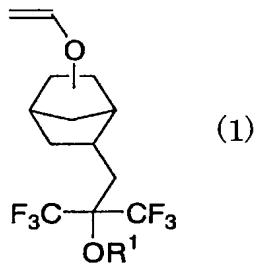
As a result of an eager examination, the present inventors have found that copolymers using fluorine-containing vinyl ethers are effective for solving the task, thereby reaching the present invention. Specifically, it was found that specific fluorine-containing vinyl ethers are capable of copolymerizing with various acrylic-series monomers, and that the obtained fluorine-containing polymers dissolve in various organic solvents and at the same time have high transparency.

[0007]

That is, the present invention provides a fluorine-containing copolymer which is obtained by copolymerizing a fluorine-containing vinyl ether (A) represented by the general formula (1) with a monomer (B) as major monomer components, and in which the monomer (B) is at least one or two or more monomers selected from acrylic esters or methacrylic esters, and a resist material using the fluorine-containing polymer.

[0008]

[Chemical Formula 5]



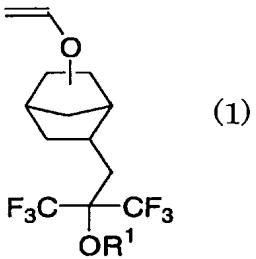
(In the formula, R¹ is -H or a C₁-C₈ alkyl group, and in the case of the alkyl group it may contain an oxygen atom.)

[0009]

5 In the following, the present invention is described in detail. The fluorine-containing vinyl ether (A), which is one of major monomer components for obtaining fluorine-containing copolymers of the present invention, is represented by the following general formula (1).

[0010]

10 [Chemical Formula 6]



(In the formula, R¹ is -H or a C₁-C₈ alkyl group, and in the case of the alkyl group it may contain an oxygen atom.)

[0011]

15 Herein, a unit derived from a hexafluoroisopropanol unit (-C(CF₃)₂-OH) improves transparency due to fluorine atoms, improves adhesion to substrate when it has turned to a polymer, and at the same time improves solubility in alkali aqueous solution upon development.

[0012]

20 The monomer (B) is at least one type selected from acrylic esters or methacrylic esters. These can be used alone or in combination of two types or more. That is, the acrylic ester or methacrylic ester usable herein is not

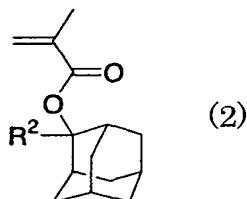
limited in structure. For example, it is possible to use halogen such as fluorine, an alkyl group optionally containing fluorine, and adamantane ring, norbornene ring, lactone ring and the like optionally having in their portion a functional group such as alcohol and carboxylic acid. It is also 5 possible to use an acrylic ester or methacrylic ester having at its side chain an alkyl group optionally having fluorine in its portion and an acrylic ester or methacrylic ester having a hexafluorocarbinol group.

[0013]

According to the present invention, it is possible to use herein an 10 acrylic ester or methacrylic ester containing an acid-labile group in order to achieve characteristics as positive-type resist. As they are exemplified, t-Bu acrylate, t-Bu methacrylate, 2-methyladamantyl acrylate, 15 2-ethyladamantyl acrylate and the like are cited. One containing an adamantane structure represented by the following general formula (2) can be shown as a preferable example since it improves etching resistance.

[0014]

[Chemical Formula 7]



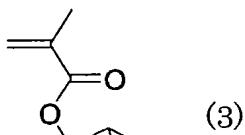
(In the formula R² is -CH₃ or -CH₂CH₃.)

20 [0015]

On the other hand, a methacrylic ester represented by the following structural formula (3) can be shown as a preferable example since it improves etching resistance and adhesion to substrate.

[0016]

25 [Chemical Formula 8]



(3)

[0017]

In the ratios of the fluorine-containing vinyl ether (A) and the monomer (B) in the fluorine-containing copolymer of the present invention, 5 an arbitrary range is selected without a particular limitation. It is, however, preferable that the fluorine-containing polymer contain 0.1 mol% or greater of a unit based on the fluorine-containing vinyl ether (A) and the monomer (B) in order that the fluorine-containing polymer of the present invention shows high transparency and high resolution. More preferably, 10 the content is 1 mol% or greater.

[0018]

Other monomers can be copolymerized, as long as capacity of the fluorine-containing copolymer of the present invention is not impaired. Furthermore, several kinds can be used in combination. As they are 15 exemplified, α -olefins (e.g., ethylene and propylene), cyclic olefins (e.g., norbornene and cyclohexene), vinyl ethers other than that of the invention, vinyl esters, acrylic or methacrylic acid, acrylic or methacrylic ester, α -trifluoromethylacrylic acid, α -trifluoromethylacrylic ester, allyl ether, styrene, vinyl silane, anhydrous maleic acid, acrylonitrile and the like are 20 cited. They may contain fluorine atoms, heteroatoms (e.g., oxygen), functional groups, cyclic structure organic groups (e.g., adamantyl group), and reactive groups that are released by the action of acid. Furthermore, it is possible to use fluoroolefins such as tetrafluoroethylene, chlorotrifluoroethylene, hexafluoroisobutene, hexafluoropropylene, 25 trifluoroethylene, perfluorovinyl ether, and octafluorocyclopentene.

[0019]

In the ratios of other monomers in the copolymer, an arbitrary range is selected without particular limitation. Other monomer components are preferably 98 mol% or less, since it is preferable that the units based on the fluorine-containing vinyl ether (A) and the monomer (B), which are main 5 components of the fluorine-containing copolymer of the present invention, are each contained in 1 mol% or greater.

[0020]

In number average molecular weight of the fluorine-containing polymer of the present invention, a range of 1,000 to 1,000,000 is generally 10 appropriate. A range of 2,000 to 100,000 is preferably appropriate. If the molecular weight is less than that, it is insufficient in strength as polymer and inferior in heat resistance in the use as various materials. If the molecular weight is greater than 100,000, it is inferior in solubility in solvent.

15 [0021]

The process of producing the fluorine-containing polymer of the present invention is not particularly limited. A known process such as anionic polymerization, radical polymerization, cation polymerization or coordination polymerization is used. Preferably, radical polymerization is 20 used. As the polymerization manner then, a known method such as bulk polymerization, solution polymerization, suspension polymerization or emulsion polymerization can be used. The temperature of the polymerization reaction can be suitably set depending on the polymerization process, polymerization manner, the type of the polymerization initiator, and the like. Specifically, it is 20-200°C, preferably 40-120°C. Examples 25 of the radical polymerization initiator are not particularly limited. As examples, azo-series compounds, peroxide-series compounds and redox-series compounds are cited.

[0022]

30 Solvent may be used in the polymerization reaction upon producing the fluorine-containing polymer of the present invention. Although the

solvent is not particularly limited, it is preferably one that does not greatly interfere with the polymerization. Its examples are ketone-series solvents such as acetone; aromatic-series solvents such as toluene; hydrocarbon-series solvents such as cyclohexane; alcohol-series solvents such as isopropyl alcohol; ester-series solvents such as butyl acetate; and ether-series solvents such as tetrahydrofuran. Furthermore, it is possible to use a molecular weight adjusting agent, such as mercaptan, together therewith.

[0023]

As the emulsifying agent upon conducting the emulsion polymerization, it is possible to use an anion or nonion emulsifying agent or both. Although the radical initiator then is not particularly limited, a water-soluble initiator such as persulfate can preferably be used.

[0024]

The suspension stabilizer upon conducting the suspension polymerization is not particularly limited. It is possible to use a generally used, water-soluble polymer such as methylcellulose. That is, the fluorine-containing polymer of the present invention becomes useful as a resist material for producing semiconductors.

[0025]

[Embodiments of the Invention]

In resist materials according to the present invention, the method of using the fluorine-containing polymer in the present invention is not particularly limited. As its example, it is applied as a polymer compound that changes solubility in alkali aqueous solution by the generation of acid or amine. Its type can be applied to both of positive-type and negative-type. As an acid-labile group usable then, its object is achieved by introducing it into the fluorine-containing vinyl ether or the copolymerization component or by introducing it into them in combination. Then, a resist can be constituted by an organic solvent, a photoacid generator and an additive in addition to the fluorine-containing polymer in the present invention. It is

possible to mix other polymers into the solution by an arbitrary ratio to use a resin blend.

[0026]

Organic solvent dissolves the fluorine-containing polymer in the
5 present invention to make it into a coating material. Although the organic solvent is not particularly limited, its examples are ketones such as acetone and methyl ethyl ketone; polyhydric alcohols and their derivatives such as ethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, and propylene glycol monomethyl ether acetate; ethers such as
10 tetrahydrofuran and dioxane; esters such as ethyl acetate, butyl acetate, methyl lactate, and ethyl lactate; aromatic solvents such as xylene and toluene; and fluorine-series solvents such as fleon. These can be used alone or in combination.

[0027]

15 The photoacid generator is not particularly limited. It can be used by selecting an arbitrary one from those used as acid generators of chemically amplified resists. As examples of such acid generator, bisulfonyldiazomethanes, nitrobenzyl derivatives, onium salts, halogen-containing triazine compounds, cyano group-containing
20 oximesulfonate compounds, and other oximsulfonate compounds are cited. These acid generators may be used alone or may be used in combination of at least two types. Its content is generally used in a range of 0.5-20 parts by weight relative to 100 parts by weight of the polymer compound. Examples of other additives are solubility inhibitor, plasticizer, stabilizer,
25 coloring agent, light amplifier, surfactant, tackifier, leveling agent, defoaming agent, adhesion enhancing agent, quencher, and the like.

[0028]

The use of a resist material of the present invention can be conducted by a method similar to conventional photoresist techniques. For
30 example, in case that the fluorine-containing polymer of the present invention is applied as a polymer compound that changes solubility in alkali

aqueous solution by acid generation, a solution of resist composition is applied to a silicon wafer by spin coating, followed by drying and film formation, and this is irradiated with a pattern through a mask by a light exposure apparatus. By subjecting this to heating and alkali development,
5 a desired pattern can be formed on the resin layer.

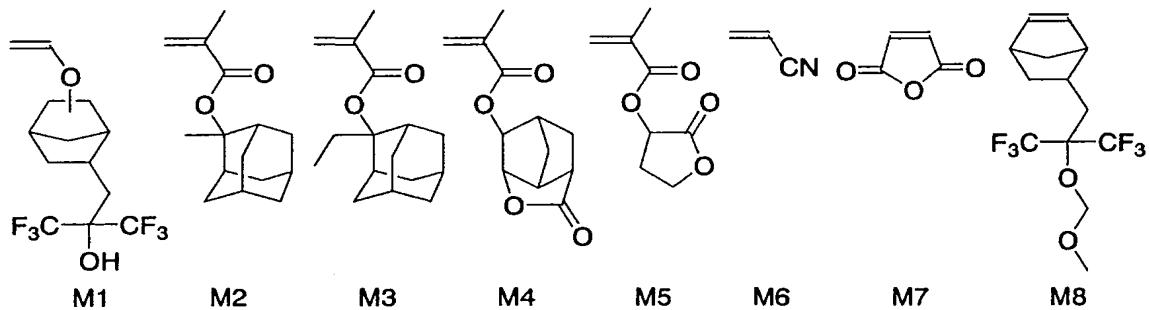
[0029]

[Examples]

Next, the present invention is described in more detail by examples. Monomer structural formulas used in respective examples are shown in the
10 following.

[0030]

[Chemical Formula 9]



[0031]

15 [Example 1]

A 50mL glass container was charged with 5.0g of the above shown M1, 1.58g of M2, 0.16g of di-t-butylperoxypivalate, and 6.6g of butyl acetate, followed by replacing the inside of the container with nitrogen. Then, the reaction was conducted, while the reaction container was maintained at
20 60°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid with 1L of n-hexane, followed by filtration and vacuum drying, thereby obtaining 3.7g of a white-color polymer. The weight average molecular weight of polystyrene conversion determined by GPC measurement (GPC SYSTEM-11 made by Shodex) of the obtained polymer was 25,400. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm

wavelength of 100nm thickness conversion of a coating film made from the solution was 98%.

[0032]

[Example 2]

5 A 50mL glass container was charged with 5.0g of the above-shown M1, 1.67g of M3, 0.23g of di-t-butylperoxypivalate, and 6.7g of butyl acetate, followed by replacing the inside of the container with nitrogen. Then, the reaction was conducted, while the reaction container was maintained at 60°C for 20hr. After the reaction, a polymer was reprecipitated from the
10 cooled reaction liquid with 1L of n-hexane, followed by filtration and vacuum drying, thereby obtaining 3.5g of a white-color polymer. The weight average molecular weight of the obtained polymer was 20,100. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm
15 thickness conversion of a coating film made from the solution was 97%.

[0033]

[Example 3]

A 50mL glass container was charged with 2.5g of the above-shown M1, 1.84g of M2, 0.88g of M4, 0.20g of azobisisobutyronitrile, and 26g of toluene, followed by replacing the inside of the container with nitrogen.
20 Then, the reaction was conducted, while the container was maintained at 65°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid with 1L of n-hexane, followed by filtration and vacuum drying, thereby obtaining 3.4g of a white-color polymer. The weight average molecular weight of the obtained polymer was 15,000.
25 Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 95%.

[0034]

30 [Example 4]

A 50mL glass container was charged with 2.5g of the above-shown

M1, 1.84g of M2, 0.21g of M6, 0.20g of azobisisobutyronitrile, and 23g of toluene, followed by replacing the inside of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 65°C for 20hr. After the reaction, a polymer was reprecipitated from the 5 cooled reaction liquid with 1L of n-hexane, followed by filtration and vacuum drying, thereby obtaining 3.4g of a white-color polymer. The weight average molecular weight of the obtained polymer was 19,000. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm 10 thickness conversion of a coating film made from the solution was 96%.

[0035]

[Example 5]

A 50mL glass container was charged with 2.5g of the above-shown M1, 1.84g of M2, 0.77g of M7, 0.20g of azobisisobutyronitrile, and 26g of toluene, followed by replacing the inside of the container with nitrogen. 15 Then, the reaction was conducted, while the container was maintained at 65°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid with 1L of n-hexane, followed by filtration and vacuum drying, thereby obtaining 3.1g of a white-color polymer. The weight average molecular weight of the obtained polymer was 13,000. 20 Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 96%.

[0036]

25 [Example 6]

A 50mL glass container was charged with 2.5g of the above-shown M1, 0.53g of M5, 1.50g of M8, 0.20g of azobisisobutyronitrile, and 23g of toluene, followed by replacing the inside of the container with nitrogen. Then, the reaction was conducted, while the container was maintained at 30 65°C for 20hr. After the reaction, a polymer was reprecipitated from the cooled reaction liquid with 1L of n-hexane, followed by filtration and

vacuum drying, thereby obtaining 2.7g of a white-color polymer. The weight average molecular weight of the obtained polymer was 8,000. Furthermore, the obtained polymer was soluble in propylene glycol monomethylacetate. Light transmittance at 193nm wavelength of 100nm thickness conversion of a coating film made from the solution was 99%.

5 [0037]

[Example 7]

The polymer obtained in Example 3 was dissolved in propylene glycol monomethyl ether acetate to have a solid matter concentration of 10wt%. Then, triphenylsulfonium triflate made by Midori Kagaku Co., Ltd. as an acid generator was dissolved to be in an amount of 2 parts by weight per 100 parts by weight of the polymer, followed by filtration with 0.2 micron membrane filter, thereby preparing a resist solution. This was applied to a silicon wafer by spin coating to obtain a resist film having a thickness of 500nm. After a preliminary baking at 110°C, a light exposure was conducted at 193nm with an ArF excimer laser, and then a post exposure baking was conducted at 120°C. Then, a development was conducted by a puddle method at 23°C for 1 minute using 2.38 wt% tetramethylammonium hydroxide aqueous solution, followed by washing with pure water and drying. As a result, the laser non-exposed portion was not dissolved by the tetramethylammonium hydroxide aqueous solution, but the laser-exposed portion was completely dissolved. Thus, a necessary positive-type behavior required as resist was observed.

20 [0038]

25 [Advantageous Effect of the Invention]

A fluorine-containing copolymer of the present invention has characteristics that light scattering and absorption are low and that solubility in solvent is superior, and becomes useful as a transparent resist material suitable for coating.

[Document Name] Abstract

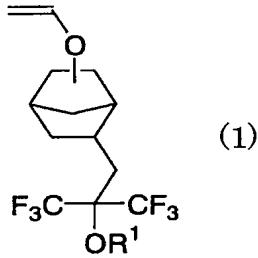
[Abstract]

[Task] It is to provide a transparent fluorine-containing copolymer that becomes a polymer material required to be low in light scattering and

5 absorption and to be high in transparency, and a resist material using the fluorine-containing copolymer.

[Solving Means] A fluorine-containing copolymer which is obtained by copolymerizing a fluorine-containing vinyl ether (A) represented by the general formula (1) with a monomer (B) as major monomer components, and
10 in which the monomer (B) is at least one or two or more monomers selected from acrylic esters or methacrylic esters.

[Chemical Formula 1]



(In the formula, R¹ is -H or a C₁-C₈ alkyl group, and in the case of the alkyl

15 group it may contain an oxygen atom.) A fluorine-containing copolymer of the present invention is superior in solubility in solvent and transparency.

[Selected Drawing] None